

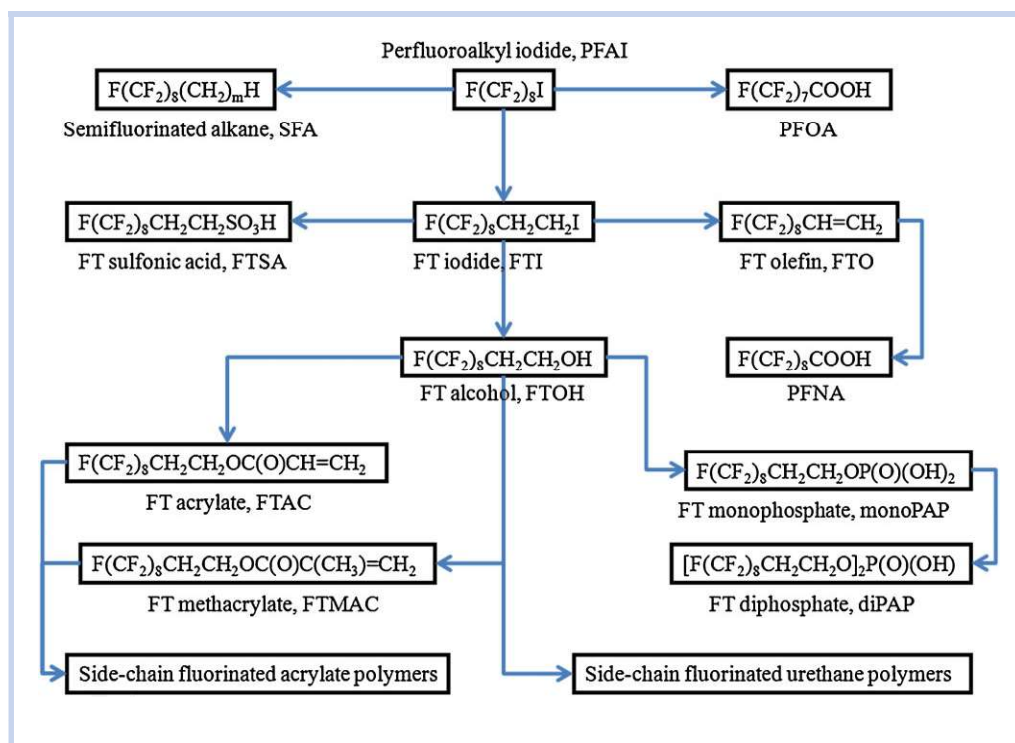


Figure 3. Perfluoroalkyl carboxylic acids and fluorotelomer (FT) derivatives synthesized from perfluoroalkyl iodides (PFAIs), exemplified for a starting PFAI with 8 C atoms. N.B. Names and acronyms for substance families are indicated. Those for the specific compounds shown can be found in the Supplemental Data.

uses for individual PFASs, as well as their environmental occurrence, for a better understanding of their environmental origin and how certain families and substances are related to one another. Another key point of the discussion is the likelihood that any or all members of PFAS groups have the ability to transform to the long-chain perfluorinated acids, provided, of course, that they have a long enough perfluoroalkyl moiety. A more comprehensive compilation of individual substances is given in the Supplemental Data, which also includes CAS registry numbers when assigned.

First, we choose to make a fundamental distinction in substances by dividing them into 2 primary categories: nonpolymers and polymers (Figure 4). It is well accepted that polymers generally have very different physical, chemical, and biological properties than discrete chemical substances of low molecular weight (e.g., methyl methacrylate versus poly[methyl methacrylate]). There are various definitions of a polymer, but the basic concept describes a substance consisting of molecules characterized by the sequence of one or more types of monomer unit. Precise criteria for distinguishing polymers from nonpolymers have been established, for instance, under the European Union REACH legislation (ECHA 2008).

Nonpolymer perfluoroalkyl and polyfluoroalkyl substances

Perfluoroalkyl acids. Perfluoroalkyl acids (PFAAs) occupy a prominent place in the literature on PFASs. The family of PFAAs includes perfluoroalkyl carboxylic, sulfonic, sulfinic, phosphonic, and phosphinic acids (Table 2). PFAAs are important both because they are highly persistent substances that have been directly emitted to the environment or are formed indirectly from the environmental degradation or

metabolism of precursor substances, and because they (or their salts) are or have been used in a wide variety of industrial and consumer applications. Depending on their acid strength (pK_a value), PFAAs will dissociate to a greater or lesser extent to their anions in aqueous environmental media, soils, or sediments. The protonated and anionic forms have very different physicochemical properties. For instance, the perfluorooctanoate anion is highly water-soluble and has negligible vapor pressure, whereas perfluorooctanoic acid has very low water solubility and sufficient vapor pressure to partition out of water into air (Kaiser et al. 2005; Kaiser et al. 2006; Webster and Ellis 2010; Webster et al. 2010). However, for perfluoroalkyl carboxylic acids, there is an ongoing debate regarding what is the environmentally relevant pK_a , with measured and estimated values varying by several log units for PFOA (Burns et al. 2008; Goss 2008; Cheng et al. 2009; Rayne and Forest 2010a).

Perfluoroalkyl carboxylic acids: Perfluoroalkyl carboxylic acids (PFCAs; Table 2), also known as perfluorocarboxylic acids or perfluoroalkanoic acids, have the general chemical formula $C_nF_{2n+1}COOH$. The most frequently discussed PFCA is PFOA, $C_7F_{15}COOH$. The ammonium salt of PFOA, ammonium perfluorooctanoate (APFO, $NH_4^+ C_7F_{15}COO^-$) has been used for many decades as an essential “processing aid” in the manufacture of fluoropolymers such as polytetrafluoroethylene, by the dispersion (or emulsion) process (Kissa 1994; Fluoropolymer Manufacturing Group 2001). A chemically inert perfluorinated surfactant is chosen for this application to avoid reaction of the growing free-radical polymer chains with the processing aid, which would lead to a lowering of the molecular weight of the polymer produced. APFO and derivatives of it were also produced and marketed for fluorosurfactant use (3M Company 2000a). Between 1947

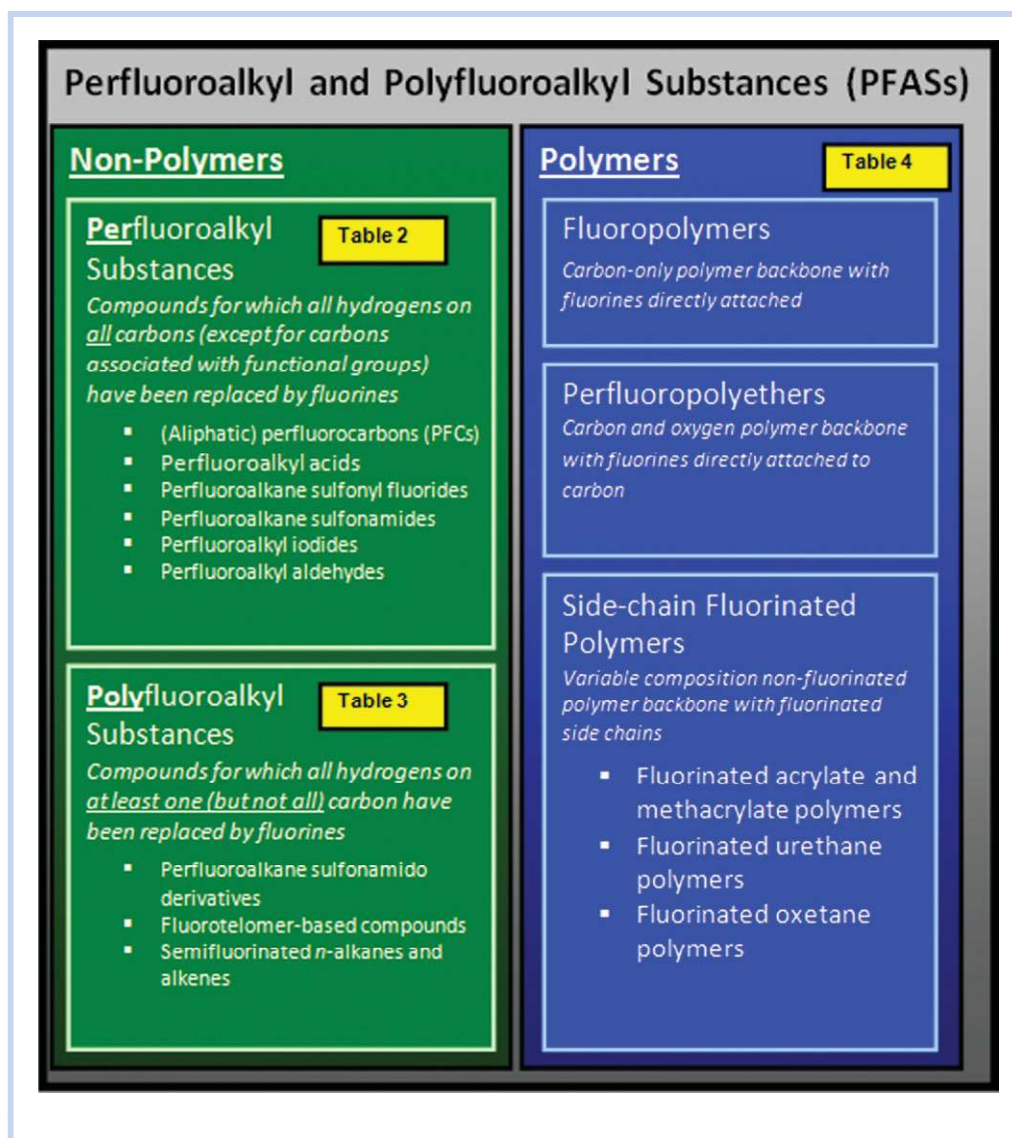


Figure 4. Classification hierarchy of environmentally relevant perfluoroalkyl and polyfluoroalkyl substances (PFASs).

and 2002, APFO was manufactured by multiple companies around the world, probably mainly or exclusively by ECF of octanoyl fluoride. In 2002, the major global historic APFO manufacturer ceased its production (3M Company 2000a, 2000c). Thus, in addition to continued ECF-based APFO production from the remaining ECF producers, a process in which linear perfluorooctyl iodide (PFOI) synthesized by telomerization is converted into PFOA was brought on-stream in late 2002 to meet the need for this critical raw material (Prevedouros et al. 2006). This new telomerization-based process leads to only linear PFOA, whereas the ECF process produces a mixture of linear (70%–80%) and branched PFOA isomers.

Perfluorononanoic acid, $C_8F_{17}COOH$ (PFNA) has also been manufactured and used (from 1975 onward) as its ammonium salt, $NH_4^+ C_8F_{17}COO^-$ (APFN), principally for producing fluoropolymer dispersions, especially polyvinylidene fluoride (PVDF) (Prevedouros et al. 2006). It has also been marketed for general use as a fluorinated surfactant. A sample of commercial “APFN,” known as Surflon[®] S-111, has been analyzed and shown to contain significant propor-

tions of the ammonium salts of longer PFCA homologues, especially those with 11 (PFUnDA) and 13 (PFTrDA) C atoms, which amounted to 20 and 5 weight percent of the mixture, respectively (Prevedouros et al. 2006; in the supporting information). The presence of these homologues with 2 and 4 additional C atoms, as confirmed by an industrial user (van der Putte et al. 2010), indicates that Surflon[®] S-111 is derived from a mixture of fluorotelomer-based precursors and, hence, suggests that it is constituted, predominantly or exclusively, of linear isomers. These conclusions are consistent with patents that claim manufacture of PFNA from telomer-based raw materials, namely by the oxidation of 8:2 fluorotelomer olefin, $C_8F_{17}CH=CH_2$ (Ukihashi et al. 1977; Aoyama and Chiba 1997) or by the carboxylation of $C_8F_{17}I$ (Nagasaki et al. 1988). The APFN commercial mixture has its own CAS Registry Number: 72968-38-8. Several publications report toxicological studies on the blend corresponding to this number, but do not provide information on the proportions or linearity of the homologues present (Mundt et al. 2007; Stump et al. 2008; Mertens et al. 2010).

Table 2. Hierarchical overview of the nonpolymer perfluoroalkyl substances, compounds for which all H atoms on all C atoms in the alkyl chain attached to the functional group have been replaced with F

Classification and chemical structure	$C_nF_{2n+1}R$, where R =	Examples	Uses
Perfluoroalkyl acids (PFAAs)			
Perfluoroalkyl carboxylic acids (PFCAs) ^a	-COOH	Perfluorooctanoic acid (PFOA), $C_7F_{15}COOH$	Surfactant
Perfluoroalkyl carboxylates (PFCAs) ^a	-COO ⁻	Perfluorooctanoate (PFOA), $C_7F_{15}COO^-$	
Perfluoroalkane sulfonic acids (PFSA) ^b	-SO ₃ H	Perfluorooctane sulfonic acid (PFOS), $C_8F_{17}SO_3H$	Surfactant
Perfluoroalkane sulfonates (PFSA) ^b	-SO ₃ ⁻	Perfluorobutane sulfonic acid (PFBS), $C_4F_9SO_3H$ Perfluorooctane sulfonate (PFOS), $C_8F_{17}SO_3^-$ Perfluorobutane sulfonate (PFBS), $C_4F_9SO_3^-$	
Perfluoroalkane sulfinic acids (PFSIA) ^b	-SO ₂ H	Perfluorooctane sulfinic acid (PFOSI), $C_8F_{17}SO_2H$	Intermediate environmental transformation product
Perfluoroalkyl phosphonic acids (PFPA) ^c	-P(=O)(OH) ₂	Perfluorooctyl phosphonic acid (C8-PFPA) $C_8F_{17}P(=O)(OH)_2$	Surfactant
Perfluoroalkyl phosphinic acids (PFPIA) ^c	-P(=O)(OH)(C _m F _{2m+1})	Bis(perfluorooctyl) phosphinic acid (C8/C8-PFPIA) $C_8F_{17}P(=O)(OH)(C_8F_{17})$	Surfactant
Perfluoroalkane sulfonyl fluorides (PASFs) ^b	-SO ₂ F	Perfluorooctane sulfonyl fluoride (POSF), $C_8F_{17}SO_2F$	Major raw material for surfactant and surface protection products
Perfluoroalkane sulfonamides (FASAs) ^b	-SO ₂ NH ₂	Perfluorobutane sulfonyl fluoride (PBSF), $C_4F_9SO_2F$ Perfluorooctane sulfonamide (FOSA), $C_8F_{17}SO_2NH_2$	Major raw material for surfactant and surface protection products
Perfluoroalkanyl fluorides (PAFs) ^b	-COF	Perfluorooctanyl fluoride (POF), $C_7F_{15}COF$	Major raw material for PFOA made by the ECF process; raw material for surfactant and surface protection products
Perfluoroalkyl iodides (PFAIs) (Telomer A) ^c	-I	Perfluorohexyl iodide (PFHxI), $C_6F_{13}I$	Major raw material for surfactant and surface protection products
Perfluoroalkyl aldehydes (PFALs) and aldehyde hydrates (PFAL-H ₂ O) ^c	-CHO and -CH(OH) ₂	Perfluorononanal (PFNAL), $C_8F_{17}CHO$	Intermediate environmental transformation product

^aSubstances originating by either electrochemical fluorination (ECF) or fluorotelomer processes;^bSubstances originating by the ECF process;^cSubstances originating by the fluorotelomer process.

Table 3. Hierarchical overview of the nonpolymer polyfluoroalkyl substances: compounds for which all H atoms on at least one (but not all) C atoms have been replaced with F

	Classification and chemical structure	$C_nF_{2n+1}R$, where $R =$	Examples	Uses
Perfluoroalkane sulfonamido substances ^a	<i>N</i> -Alkyl perfluoroalkane sulfonamides (MeFASAs, EtFASAs, BuFASAs)	$-SO_2NH(R')$ where $R' = C_mH_{2m+1}$ ($m = 1, 2, 4$)	<i>N</i> -Methyl perfluorooctane sulfonamide (MeFOSA), $C_8F_{17}SO_2N(CH_3)H$	Major raw material for surfactant and surface protection products
			<i>N</i> -Ethyl perfluorobutane sulfonamide (EtFBSA), $C_4F_9SO_2N(C_2H_5)H$	
			<i>N</i> -Butyl perfluorooctane sulfonamide (BuFOSA), $C_8F_{17}SO_2N(C_4H_9)H$	
	Perfluoroalkane sulfonamidoethanols (FASEs) and <i>N</i> -alkyl perfluoroalkane sulfonamidoethanols (MeFASEs, EtFASEs, BuFASEs)	$-SO_2N(R')CH_2CH_2OH$ where $R' = C_mH_{2m+1}$ ($m = 0, 1, 2, 4$)	Perfluorooctane sulfonamidoethanol (FOSE), $C_8F_{17}SO_2NHCH_2CH_2OH$	Major raw material for surfactant and surface protection products
			<i>N</i> -Ethyl perfluorobutane sulfonamidoethanol (EtFBSE), $C_4F_9SO_2N(C_2H_5)CH_2CH_2OH$	
Fluorotelomer substances ^b	<i>N</i> -Alkyl perfluoroalkane sulfonamidoethyl acrylates and methacrylates (MeFAS(M)ACs, EtFAS(M)ACs, BuFAS(M)ACs)	$-SO_2N(R')CH_2CH_2O-C(O)CH=CH_2$ and $-SO_2N(R')CH_2CH_2O-C(O)C(CH_3)=CH_2$ where $R' = C_mH_{2m+1}$ ($m = 1, 2, 4$)	<i>N</i> -Ethyl perfluorooctane sulfonamidoethyl acrylate (EtFOSAC), $C_8F_{17}SO_2N(C_2H_5)CH_2CH_2O-C(O)CH=CH_2$	Major raw material for surfactant and surface protection products
	Perfluoroalkane sulfonamidoacetic acids (FASAAAs) and <i>N</i> -alkyl perfluoroalkane sulfonamidoacetic acids (MeFASAAAs, EtFASAAAs, BuFASAAAs)	$-SO_2N(R')CH_2COOH$ where $R' = C_mH_{2m+1}$ ($m = 0, 1, 2, 4$)	<i>N</i> -Ethyl perfluorooctane sulfonamidoacetic acid (EtFOSAAA), $C_8F_{17}SO_2N(C_2H_5)CH_2CO_2H$	Intermediate environmental transformation product
	Semifluorinated <i>n</i> -alkanes (SFAs) and alkenes (SFAenes)	$-(CH_2)_mH$ and $-CH=CH(CH_2)_{m-2}H$, with $m = 2-16$ and $n = 6-16$	Perfluorohexylhexadecane (F_6H_{16}), $F(CF_2)_6(CH_2)_{16}H$	Ski wax; medical applications
	<i>n</i> :2 Fluorotelomer iodides (<i>n</i> :2 FTIs) (Telomer B)	$-CH_2CH_2I$	8:2 Fluorotelomer iodide (8:2 FTI), $C_8F_{17}CH_2CH_2I$	Major raw material for surfactant and surface protection products
	<i>n</i> :2 Fluorotelomer olefins (<i>n</i> :2 FTOs)	$-CH=CH_2$	6:2 Fluorotelomer olefin (6:2 FTO), $C_6F_{13}CH=CH_2$	Raw material for surfactant and surface protection products
	<i>n</i> :2 Fluorotelomer alcohols (<i>n</i> :2 FTOHs)	$-CH_2CH_2OH$	10:2 Fluorotelomer alcohol (10:2 FTOH), $C_{10}F_{21}CH_2CH_2OH$	Major raw material for surfactant and surface protection products
	<i>n</i> :2 Unsaturated fluorotelomer alcohols (<i>n</i> :2 FTUOHs)	$-CF=CHCH_2OH$	8:2 Unsaturated fluorotelomer alcohol (8:2 FTUOH), $C_7F_{15}CF=CHCH_2OH$	Intermediate environmental transformation product
	<i>n</i> :2 Fluorotelomer acrylates (<i>n</i> :2 FTACs) and methacrylates (<i>n</i> :2 FTMACs)	$-CH_2CH_2OC(O)CH=CH_2$ and $-CH_2CH_2OC(O)C(CH_3)=CH_2$	8:2 Fluorotelomer acrylate (8:2 FTAC), $C_8F_{17}CH_2CH_2OC(O)CH=CH_2$ 6:2 Fluorotelomer methacrylate (6:2 FTMAC), $C_6F_{13}CH_2CH_2O-C(O)C(CH_3)=CH_2$	Major raw material for fluorotelomer-based polymers used in surface protection products
	<i>n</i> :2 Polyfluoroalkyl phosphoric acid esters, polyfluoroalkyl phosphates, fluorotelomer phosphates (PAPs)	$-(CH_2CH_2O)_xP(=O)(OH)_{3-x}$ where $x = 1$ or 2	8:2 Fluorotelomer phosphate monoester (8:2 monoPAP), $C_8F_{17}CH_2CH_2OP(=O)(OH)_2$ 8:2 Fluorotelomer phosphate diester (8:2 diPAP), $(C_8F_{17}CH_2CH_2O)_2P(=O)OH$	Surfactant and surface protection products

(Continued)

Table 3. (Continued)

	Classification and chemical structure	$C_nF_{2n+1}R$, where R =	Examples	Uses
	n:2 Fluorotelomer aldehydes (n:2 FTALs) and unsaturated aldehydes (n:2 FTUALs)	$-CH_2CHO$ and $-CF=CHCHO$	8:2 Fluorotelomer aldehyde (8:2 FTAL), $C_8F_{17}CH_2CHO$ 8:2 Fluorotelomer unsaturated aldehyde (8:2 FTUAL), $C_7F_{15}CF=CHCHO$	Intermediate environmental transformation product
	n:2 Fluorotelomer carboxylic acids (n:2 FTCAs) and unsaturated carboxylic acids (n:2 FTUCAs)	$-CH_2COOH$ and $-CF=CHCOOH$	8:2 Fluorotelomer carboxylic acid (8:2 FTCA), $C_8F_{17}CH_2COOH$ 8:2 Fluorotelomer unsaturated carboxylic acid (8:2 FTUCA), $C_7F_{15}CF=CHCOOH$	Intermediate environmental transformation product
	n:3 Saturated acids (n:3 Acids) and n:3 Unsaturated acids (n:3 UAcids)	$-CH_2CH_2COOH$ and $-CH=CHCOOH$	7:3 Acid, $C_7F_{15}CH_2CH_2COOH$ 7:3 UAcid, $C_7F_{15}CH=CHCOOH$	Intermediate environmental transformation product
	n:2 Fluorotelomer sulfonic acids (n:2 FTSAs)	$-CH_2CH_2SO_3H$	8:2 Fluorotelomer sulfonic acid (8:2 FTSa), $C_8F_{17}CH_2CH_2SO_3H$	Surfactant and environmental transformation product
Miscellaneous	Polyfluoroalkyl ether carboxylic acids	For example: $-O(C_mF_{2m})OCHF(C_pF_{2p})COOH$	4,8-Dioxa-3H-perfluorononanoate, $CF_3OCF_2CF_2CF_2OCHF_2COOH$	Alternative fluoropolymer processing aid (as ammonium salt)

^aSubstances originating by electrochemical fluorination (ECF) process;^bSubstances originating by fluorotelomer process.

In addition to their major commercial use as fluoropolymer processing aids and numerous industrial and consumer applications (Kissa 2001; Prevedouros et al. 2006), PFCAs are also the terminal degradation products from abiotic and biotic degradation of certain precursor PFASs. Such precursors include fluorotelomer alcohols (Hagen et al. 1981; Dinglasan et al. 2004; Ellis et al. 2004; Hurley et al. 2004; Wang et al. 2009; Liu et al. 2010), fluorotelomer acrylates (Butt et al. 2009; Butt et al. 2010b), fluorotelomer iodides (Young et al. 2008), fluorotelomer olefins (Nakayama et al. 2007), *N*-alkyl perfluoroalkane sulfonamides (Tomy, Tittlemier, et al. 2004; Martin et al. 2006; Plumlee et al. 2009), *N*-alkyl perfluoroalkane sulfonamidoethanols (D'eon et al. 2006; Plumlee et al. 2009), and polyfluoroalkyl phosphates (D'eon and Mabury 2007; Lee et al. 2010). Short-chain PFCAs (e.g., trifluoroacetic and pentafluoropropionic acids) may also be formed in the atmospheric degradation of certain hydrochlorofluorocarbons, hydrofluorocarbons, and fluorinated anesthetics (Boutonnet et al. 1999; Young and Mabury 2010) and perfluoro-2-methyl-3-pentanone (Jackson et al. 2011), as well as in the oxidative thermolysis of fluorinated polymers (Ellis et al. 2001). Yet, the quantitative attribution of sources of these short-chain PFCAs in the environment remains uncertain, and it is quite possible that further precursors will be identified. PFCA yields and rates of formation vary depending on the precursor substance and degradation conditions. Moreover, PFCAs and potential PFCA precursors, such as residual raw materials, may be present as impurities in commercial PFAS-based products (Washburn et al. 2005; Berger and Herzke 2006; Dinglasan-Panlilio and Mabury 2006; Larsen et al. 2006; Prevedouros et al. 2006; Schulze and Norin 2006; D'eon and Mabury 2007; Jensen et al. 2008; Fiedler et al. 2010). It was estimated that the majority (~80%) of PFCAs have been released to the

environment from fluoropolymer manufacture and use (Prevedouros et al. 2006). This percentage is, however, an overall value, heavily weighted toward the PFCAs with the greatest emissions, namely PFOA and (to a much lesser extent) PFNA. PFCAs with shorter or longer chain lengths are not known to arise primarily from fluoropolymer manufacture and use. Although in the same study (Prevedouros et al. 2006), indirect sources of PFOA and PFNA were estimated to be much less important than direct sources, there were larger uncertainties associated with the calculations for indirect sources and some recently identified precursors (e.g., polyfluoroalkyl phosphates) were excluded.

In 2006, 8 major global companies signed on to the USEPA "2010/2015 PFOA Stewardship Program" (USEPA 2006b) with commitments first to reduce emissions and product content of PFOA, higher homologues and precursors by 95% by 2010 and second to work toward the elimination of PFOA, higher homologues, and precursors by 2015. Companies have reported significant progress toward achieving these goals (Ritter 2010). Interestingly, coincident with these changes, there have been reports showing significantly increased levels of perfluorobutanoic acid (PFBA) in water (Möller et al. 2010) and air (Weinberg et al. 2011b) that are most likely associated with the conversion to shorter chain perfluoroalkyl products.

Perfluoroalkane (or -alkyl) sulfonic acids: Perfluoroalkyl sulfonic acids, $C_nF_{2n+1}SO_3H$ (PFASs, Table 2), are the 2nd major PFAA family of significance. The alternative name perfluoroalkane sulfonic acid has been used most commonly in the literature, in line with IUPAC recommendations, and we will adopt it here. Perfluorooctane sulfonic acid $C_8F_{17}SO_3H$ (PFOS), is the PFSA that has commanded greatest attention beginning when it was first detected

Table 4. Hierarchical overview of fluoropolymers, perfluoropolyethers, and side-chain-fluorinated polymers

		Example(s)	Uses
Fluoropolymers: Carbon-only polymer backbone with F directly attached to backbone C atoms		$-(CF_2CF_2)_n-$ Polytetrafluoroethylene (PTFE) $-(CH_2CF_2)_n-$ Polyvinylidene fluoride (PVDF) $-(CH_2CHF)_n-$ Polyvinyl fluoride (PVF) $-(CF_2CF_2)_n-(CF(CF_3)CF_2)_m-$ Fluorinated ethylene propylene (FEP)	Plastics
Perfluoropolyethers (PFPEs): Ether polymer backbone with F atoms directly attached		Examples: $F-(C_mF_{2m}O-)_nCF_3$ $HOCH_2O-[C_mF_{2m}O-]_nCH_2OH$ -where $C_mF_{2m}O$ represents $-CF_2O-$, $-CF_2CF_2O-$, and/or $-CF(CF_3)CF_2O-$ units distributed randomly along the polymer backbone	Functional fluids, surfactants, and surface protection products
Side-chain-fluorinated polymers: Nonfluorinated polymer backbone with fluorinated side chains, ending in $-C_nF_{2n+1}$	Fluorinated acrylate and methacrylate polymers	Acrylate: Backbone- $CH(C(O)O-X-C_nF_{2n+1})$ Methacrylate: Backbone- $C(CH_3)(C(O)O-X-C_nF_{2n+1})$ -where X is $-CH_2CH_2N(R')SO_2-$ with $R' = -C_nH_{2n+1}$ ($n = 0, 1, 2, 4$) or $-CH_2CH_2-$	Surfactants and surface protection products
	Fluorinated urethane polymers	Backbone- $NHC(O)O-X-C_nF_{2n+1}$ -where X is either $-CH_2CH_2N(R')SO_2-$ with $R' = -C_nH_{2n+1}$ ($n = 0, 1, 2, 4$) or $-CH_2CH_2-$	Surfactants and surface protection products
	Fluorinated oxetane polymers	Backbone- CH_2OCH_2-R -where $R = -CF_3$, $-C_2F_5$ or $-CH_2C_4F_9$	Surfactants and surface protection products

globally in biota (Giesy and Kannan 2001) and humans (Hansen et al. 2001). Subsequently, as stated above, the production of PFOS, perfluorohexane sulfonic acid (PFHxS), perfluorodecane sulfonic acid (PFDS), and the precursors of these PFASs, was phased out by the major manufacturer in 2002 (3M Company 2000c; USEPA 2000). Nevertheless, PFOS and its derivatives are still manufactured in China (Han 2009), with a production of more than 200 tons of its precursor, perfluorooctane sulfonyl fluoride, in 2006 (Yue 2008). PFOS and related compounds have been the subject of a European Union directive restricting their production and use (European Parliament 2006b). Furthermore, PFOS has been classified as a persistent, bioaccumulative, and toxic substance (OECD 2002) and was recently added to Annex B (requiring use restrictions) of the Stockholm Convention list of persistent organic pollutants (UNEP 2009). Formerly, PFOS had a number of industrial and commercial applications (3M Company 1999; Kissa 2001; Brooke et al. 2004; Paul et al. 2009). However, the environmental and toxicological significance of PFOS, ubiquitous in the global environment, also results from its presence as an impurity in and formation from perfluorooctane sulfonamido precursor substances (3M Company 1999, 2000a; Lange 2000, 2001; Xu et al. 2004; Boulanger et al. 2005; D'eon et al. 2006; Rhoads et al. 2008; Xie et al. 2009) used in vastly greater quantities (Brooke et al. 2004; Paul et al. 2009). The global commercial production of PFOS and related compounds has, to our knowledge, been based essentially or perhaps exclusively on ECF. In this

process, the electrolysis of a solution of octane sulfonyl fluoride in anhydrous HF leads to perfluorooctane sulfonyl fluoride, $C_8F_{17}SO_2F$ (POSF), the key intermediate from which all PFOS-related products are subsequently produced (3M Company 1999; Brooke et al. 2004; Lehmler 2005; Paul et al. 2009). The resulting PFOS, the precursor POSF and other derivatives manufactured from it, e.g., perfluorooctane sulfonamido derivatives such as amides, ethanol-substituted amides, and surfactant and polymeric products therefrom, may contain up to 30% branched isomers (Reagen et al. 2007), as well as additional C chain length homologues. For example, samples of the K salt of PFOS taken from the same 3M commercial lot were analyzed by 2 laboratories and found to have a purity of only 85% to 87% (representing the sum of all K-PFOS isomers), on the account of the presence mainly of C_2 - C_{10} PFSA homologues, but also of a range of PFCAs and other impurities (Seacat et al. 2003; Arsenault et al. 2008). Shorter perfluoroalkyl chain length products, notably perfluorobutane sulfonyl-based products, have been introduced as alternatives to the previously used compounds with 6 or more perfluorinated carbons, because these shorter chain length substances do not bioaccumulate due to their rapid elimination in multiple organisms tested (Olsen et al. 2009). This substitution is a consequence of the voluntary phase-out and/or subsequent regulatory restriction of PFOS-related substances and certain homologues with 5 to 7 and 9 or 10 perfluorinated C atoms (3M Company 2000b; Federal Register 2006b). Coincident with these changes, reports have

shown significantly increased levels of perfluorobutane sulfonic acid (PFBS) in environmental waters, no doubt as a consequence of the conversion to 4-C ECF-derived perfluorobutane sulfonyl products (Eschauzier et al. 2010; Möller et al. 2010).

Perfluoroalkane (or -alkyl) sulfinic acids: Perfluoroalkane sulfinic acids, $C_nF_{2n+1}SO_2H$ (PFSIAs; Table 2), are degradation products from commercial precursor compounds containing the $C_nF_{2n+1}SO_2N<$ moiety (e.g., perfluoroalkane sulfonamido ethanols, $C_nF_{2n+1}SO_2N(R)CH_2CH_2OH$) (Lange 2000, 2001; Boulanger et al. 2005; Rhoads et al. 2008). PFSIAs have been detected in wastewater treatment plant (WWTP) effluents and in the environment (Ahrens et al. 2009b; Ahrens, Siebert, et al. 2009; Ahrens, Xie, et al. 2010).

Perfluoroalkyl phosphonic and phosphinic acids: Perfluoroalkyl phosphonic acids, $O=P(OH)_2C_nF_{2n+1}$ (PFPA; Table 2), and perfluoroalkyl phosphinic acids, $O=P(OH)(C_nF_{2n+1})(C_mF_{2m+1})$ (PFPIA; Table 2), are commercial surfactants manufactured and offered for a range of consumer and industrial uses (USEPA 2006a; Mason Chemical 2011). Blends of C_6 - C_{12} PFPA and similar PFPIA blends, with CAS numbers 68412-68-0 and 68412-69-1, respectively, have been reported to have had annual production volumes in the range of tonnes to hundreds of tonnes in 1998 and 2002 (Howard and Muir 2010), but only recently have PFPA been widely detected in environmental waters (D'eon et al. 2009b; D'eon and Mabury 2010) and PFPIA in WWTP sludge (D'eon and Mabury 2010) and human serum (Lee and Mabury 2011).

Fluorotelomer-based products. The term “fluorotelomer-based products” describes a family of raw material building blocks, surfactant and polymeric products, and degradation products that all originate from the starting fluorotelomer raw material, perfluoroalkyl iodides (PFAIs), as depicted in Figures 2 and 3. As reviewed below, the degradation of fluorotelomer-based products is a potential source of PFCAs in the environment.

Perfluoroalkyl iodides, fluorotelomer iodides, and fluorotelomer olefins: Perfluoroalkyl iodides, $C_nF_{2n+1}I$ (PFAIs; Table 2), and $n:2$ fluorotelomer iodides, $C_nF_{2n+1}CH_2CH_2I$ ($n:2$ FTIs; Table 3), are the first 2 raw materials that lead to the family of polyfluoroalkyl “fluorotelomer-based” products. Both PFAIs and $n:2$ FTIs have recently been detected in air and soil near a fluorotelomer manufacturing facility in China (Ruan et al. 2010). Fluorotelomer olefins, $C_nF_{2n+1}CH=CH_2$ (FTOs; Table 3) are synthesized by dehydrohalogenation of FTIs and may also be formed as an impurity in synthesizing fluorotelomer alcohols (FTOHs) from FTIs (Prevedouros et al. 2006). As stated above, processes for manufacturing PFNA by oxidation of 8:2 FTO have been patented and may have been used industrially. FTOs are hydrosilylated to create silanes that are used in a number of applications. FTOs have been detected in the atmosphere (Barber et al. 2007; Jahnke et al. 2007; Piekartz et al. 2007), where they degrade completely and rapidly, but are expected to form low yields of PFCAs (Young and Mabury 2010). The degradation scheme proceeds via a $C_nF_{2n+1}CHO$ perfluoroalkyl aldehyde (PFAL; Table 2) intermediate (Vésine et al. 2000; Nakayama

et al. 2007). The atmospheric transformation of FTIs probably is comparable to FTOs in the ultimate outcome, mineralization with low yield of PFCAs (typically 1%–10%), and involves both fluorotelomer aldehyde $C_nF_{2n+1}CH_2CHO$ (FTAL; Table 3) and PFAL intermediates, together with the fluorotelomer carboxylic acids, $C_nF_{2n+1}CH_2COOH$ (FTCAs; Table 3) (Young et al. 2008). FTIs may hydrolyze in natural waters (Rayne and Forest 2010c), and this transformation process would presumably lead to fluorotelomer alcohols and, hence, their degradation products, as discussed below.

Fluorotelomer alcohols and their acrylic, methacrylic, and phosphoric esters: The $n:2$ fluorotelomer alcohols, $C_nF_{2n+1}CH_2CH_2OH$ ($n:2$ FTOHs; Table 3), are key raw materials in the production of $n:2$ fluorotelomer acrylates, $C_nF_{2n+1}CH_2CH_2OC(O)CH=CH_2$ ($n:2$ FTACs) and $n:2$ fluorotelomer methacrylates, $C_nF_{2n+1}CH_2CH_2OC(O)C(CH_3)=CH_2$ ($n:2$ FTMACs) (Table 3 and Figure 3). The FT(M)AC monomers are copolymerized in an aqueous emulsion polymerization with a host of non-fluorinated acrylates and other monomers to manufacture fluorotelomer-based polymers (Rao and Baker 1994). These polymers provide water, oil, and stain repellency to textiles, leather, and paper substrates. There is extensive scientific literature on the environmental occurrence of FTOHs, particularly (but not exclusively) in air (Martin et al. 2002; Oono, Harada, et al. 2008; Oono, Matsubara, et al. 2008; Strynar and Lindstrom 2008; Jahnke et al. 2009; Mahmoud et al. 2009; Dreyer et al. 2010; Langer et al. 2010; Shoeib et al. 2010; Yoo et al. 2010; Ahrens et al. 2011; Haug et al. 2011; Shoeib et al. 2011; Yoo et al. 2011). Likewise, some FTACs (Piekartz et al. 2007; Oono, Harada, et al. 2008; Oono, Matsubara, et al. 2008; Dreyer, Weinberg, et al. 2009; Mahmoud et al. 2009; Dreyer et al. 2010; Langer et al. 2010; Weinberg et al. 2011a, 2011b) and FTMACs (Oono, Matsubara, et al. 2008) have also been detected in environmental samples. The chain lengths of these fluorotelomer derivatives may vary over a broad range. For example, FTOHs with up to 18 fluorinated C atoms have been reported as detected, but not quantified, in air from an occupational setting (Nilsson et al. 2010).

Fluorotelomer alcohol phosphate esters (Table 3) are commercial fluorinated surfactants that are made by many global suppliers by the same reactions employed for non-fluorinated phosphates and used primarily for their surface tension lowering, wetting, and leveling surfactant properties (Taylor 1999). The terminology we recommend for these substances is polyfluoroalkyl phosphoric acid monoesters (monoPAPs), $(O)P(OH)_2(OCH_2CH_2C_nF_{2n+1})$, and diesters (diPAPs), $(O)P(OH)(OCH_2CH_2C_nF_{2n+1})(OCH_2CH_2C_mF_{2m+1})$. They may also be called $n:2$ fluorotelomer monophosphates and diphosphates. These compounds have been used as grease-proofing agents for food-contact paper (D'eon and Mabury 2007; Begley et al. 2008; FDA 2009; Lee et al. 2010; Lee and Mabury 2011), often as blends of varying perfluoroalkyl chain length and as salts (e.g., of diethanolamine). One specific use of monoPAPs and diPAPs that has led to their widespread presence in the environment is as an approved defoaming adjuvant in pesticide formulations. Approval for this use has now been rescinded (Federal Register 2006a). Recently, diPAPs have been reported detected in human serum at concentrations in some cases comparable to those of PFOA and in WWTP sludge at much greater levels than PFOA (D'eon et al. 2009a; Lee and Mabury 2011).

Semifluorinated alkanes and alkenes: Diblock semifluorinated *n*-alkanes (SFAs), $F(CF_2)_n(CH_2)_mH$ (or, briefly, F_nH_m ; Table 3), are a class of chemicals that are manufactured with a wide variety of chain lengths, depending on the intended use, by adding an olefin to a perfluoroalkyl iodide followed by reductive dehalogenation (Napoli 1996). These reactions also lead to semifluorinated *n*-alkenes (SFAenes), $F(CF_2)_nCH=CH(CH_2)_{m-2}H$ (or, briefly, F_nH_{m-1} ene), as byproducts (Coe and Milner 1972). Since the 1990s, industrial mixtures of long-chain SFAs (≥ 22 C atoms) have been applied in ski waxes, because they reduce friction and repel dirt due to their extremely low surface tension (Rogowski et al. 2007). Shorter-chain SFAs are used in medicinal applications (e.g., Kirchhof et al. 2002). In fluorinated ski waxes, up to 15% of SFAs are mixed with normal paraffins. The presence of SFAs in snow and soil samples from a ski area in Sweden has recently been demonstrated (Plassmann and Berger 2010).

Degradation products of fluorotelomer alcohols and their esters: *Fluorotelomer aldehydes and acids, perfluoroalkyl aldehydes, perfluoroalkyl carboxylic acids, and so forth:* The aerobic biodegradation and metabolic degradation pathways for fluorotelomer alcohols have been well studied (Frömel and Knepper 2010). A general overview of the 8:2 FTOH aerobic biodegradation pathways is presented in Figure 5. The pathways and yields of transformation products depend on the matrix in which the environmental microbial degradation (e.g., sludge, soil) or metabolism (rat, mouse, in vivo, in vitro) takes place and the length of the perfluoroalkyl chain in the fluorotelomer alcohol (Hagen et al. 1981; Dinglasan et al. 2004; Martin et al. 2005; Wang et al. 2009; Butt et al. 2010a; Liu et al. 2010; Brandsma et al. 2011). In general, the first step in biodegradation is aerobic oxidation of the starting *n*:2 fluorotelomer alcohol to form the corresponding *n*:2 fluorotelomer aldehyde, $C_nF_{2n+1}CH_2CHO$ (*n*:2 FTAL; Table 3), a short-lived, highly reactive species. The aldehyde is rapidly oxidized to form the corresponding *n*:2 fluorotelomer carboxylic acid, $C_nF_{2n+1}CH_2COOH$ (*n*:2 FTCA; Table 3). Next, dehydrohalogenation of the acid occurs to form the corresponding *n*:2 unsaturated carboxylic acid, $C_{n-1}F_{2n-1}CF=CHCOOH$ (*n*:2 FTUCA; Table 3). The dehydrohalogenation of the starting *n*:2 fluorotelomer alcohol to form the *n*:2 unsaturated fluorotelomer alcohol, $C_{n-1}F_{2n-1}CF=CHCH_2OH$ (Table 3), and oxidation to yield the *n*:2 unsaturated fluorotelomer aldehyde, $C_{n-1}F_{2n-1}CF=CHCHO$ (*n*:2 FTUAL; Table 3), have also been observed. Thereafter, a host of transient and stable transformation products, including PFCAs, have been identified. A unique transformation product identified is a polyfluorinated carboxylic acid with the same number of total C atoms as the parent *n*:2 FTOH where the 2 F atoms of the $-CF_2-$ group directly adjacent to the $-CH_2CH_2-$ moiety have been replaced with H atoms, $C_{n-1}F_{2n-1}CH_2CH_2COOH$, and a corresponding unsaturated acid, $C_{n-1}F_{2n-1}CH=CHCOOH$ (Table 3) (Martin et al. 2005; Wang et al. 2005; Fasano et al. 2006; Wang et al. 2009; Butt et al. 2010a). For these substances, we suggest for simplicity that either the formal name of the acid be used or the simple acronyms *x*:3 Acid and *x*:3 UAcid, where the *x* ($= n - 1$) designates the number of perfluorinated carbons and “3” the number of nonfluorinated C atoms. For the remaining transformation products, we suggest adopting the naming given to these substances by the authors (e.g., Martin et al. 2005; Wang et al. 2009; Butt et al. 2010a;

Liu et al. 2010). In a sediment–water microcosm, the degradation products observed from *n*:2 FTCA substrates were the corresponding PFCAs, whereas *n*:2 FTUCAs also led to (*n* – 1):3 Acids (Myers and Mabury 2010).

In mammals, the metabolic pathways for 8:2 and 6:2 FTOHs have been well studied in vivo in rats and mice and in vitro in rats, mice, and human hepatocytes. In general, the majority of administered FTOH test substance was eliminated rapidly in urine as conjugates. Absorption, distribution, metabolism, and elimination (ADME) studies using [^{14}C]-radiolabeled FTOHs have been conducted. The characteristic degradation products observed in microbial studies, including PFCAs, as well as some of their conjugates, have been reported in urine and at trace levels in organs and tissues (Fasano et al. 2006; Nabb et al. 2007; Fasano et al. 2009). The reader is referred to the articles for greater detail on these studies.

In atmospheric degradation studies, reviewed by Young and Mabury (2010), it has been shown that oxidation of *n*:2 FTOHs also leads to the formation of *n*:2 FTALs, *n*:2 FTCAs, and perfluoroalkyl aldehydes, $C_nF_{2n+1}CHO$ (PFALs; Table 2). Low yields (typically 1%–5%) of PFCAs having the same number of perfluorinated C atoms as the parent FTOH, or fewer, down to CF_3COOH , may be expected in low- NO_x atmospheres. The PFCAs with *n* – 2 or fewer perfluorinated C atoms result from “unzipping” of the perfluoroalkyl chain, by splitting off of $C(O)F_2$ molecules from the intermediate perfluoroalkoxy radicals (Ellis et al. 2004). Nevertheless, complete mineralization to $C(O)F_2$ is the major atmospheric outcome, and the yields of PFCAs decline as atmospheric NO_x levels increase (Ellis et al. 2004; Wallington et al. 2006; Young and Mabury 2010). A simplified scheme, given in Figure 6, shows the key intermediates in the atmospheric degradation of *n*:2 FTOHs to the products mentioned above, illustrated for *n* = 8. This scheme also includes the atmospheric breakdown pathways for FTIs and FTOs, discussed above, as well as for FTACs (Butt et al. 2009), because all these fluorotelomer derivatives have part of their degradation mechanism in common. This is also likely to be the case for PFAIs (Figure 6), assuming they photolyze easily to perfluoroalkyl radicals (which add O_2 to give perfluoroalkylperoxy radicals) in the lower atmosphere, as has been demonstrated for CF_3I (Solomon et al. 1994).

It is worth noting here that the PFALs will probably exist in cloud and surface waters largely as their *gem*-diol hydrates, $C_nF_{2n+1}CH(OH)_2$ (PFAL· H_2O s; Table 2), unlike the FTALs for which the hydration equilibrium is much less favorable (Rayne and Forest 2010b). With estimated pK_a values of 9 or higher, the PFAL· H_2O s will not be ionized to any great extent under environmental conditions, whereas the corresponding hydrates formed from FTALs are even weaker acids ($pK_a > 12$) (Rayne and Forest 2010b).

The esters of FTOHs may hydrolyze abiotically or biotically to FTOHs and, hence, ultimately lead to the same range of fluorinated transformation products described above. Hydrolysis studies of mono- and polyesters and mono-urethanes containing a fluorotelomer moiety have recently been reported (Dasu et al. 2010). Moreover, as expected, characteristic FTOH degradation products were detected when rainbow trout were exposed to 8:2 FTAC through their diet (Butt et al. 2010b), and when rats were dosed with monoPAPs or diPAPs (D’eon and Mabury 2007, 2011). Both

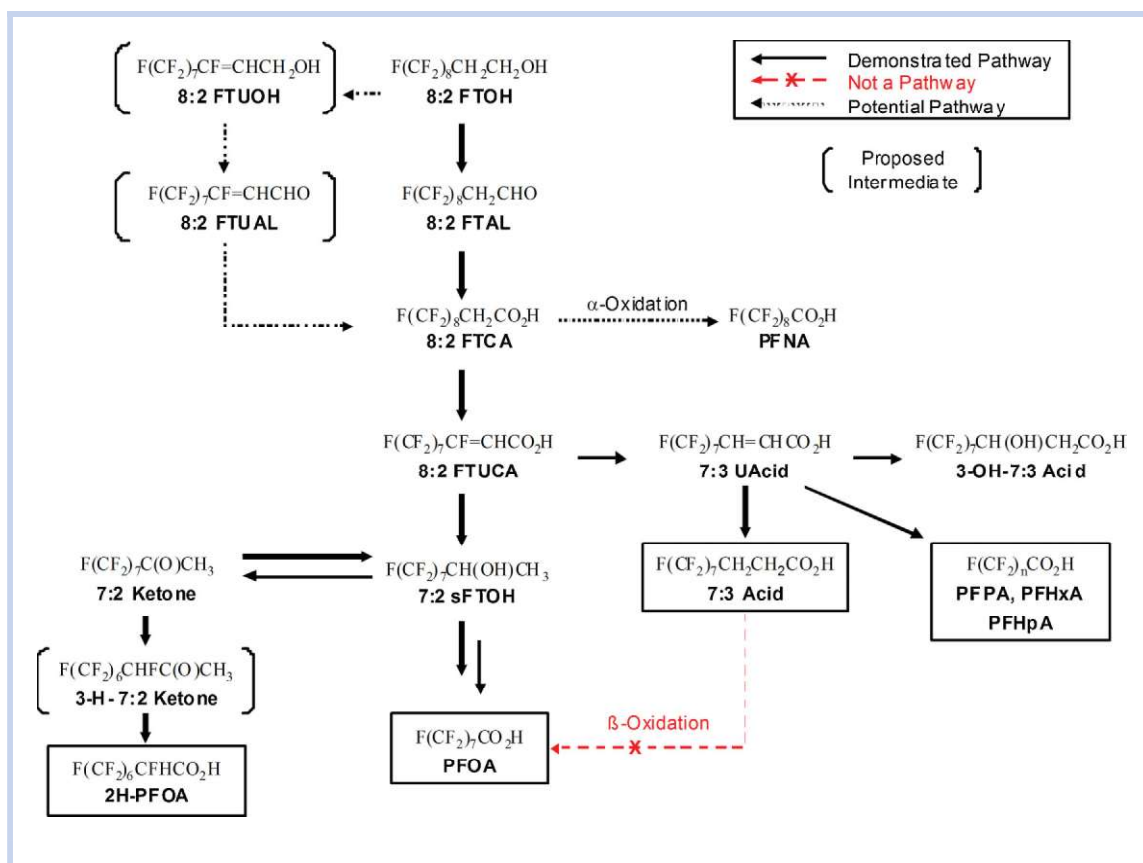


Figure 5. Aerobic biotransformation pathways for 8:2 fluorotelomer alcohol (8:2 FTOH). Adapted from Wang et al. (2009).

FTOHs and their transformation products were observed in experiments intended to simulate aerobic biodegradation of monoPAPs and diPAPs in WWTPs (Lee et al. 2010). The abiotic hydrolysis of FTACs has been predicted to have half-lives of years in marine systems but possibly only days in landfills (Rayne and Forest 2010c). Hydrolytic stability studies, conducted under OECD 111 Guidelines, on a commercial fluorotelomer-based acrylate polymer (Russell et al. 2008) and a urethane polymer (Russell et al. 2010) showed no discernible hydrolysis. Nevertheless, there is much debate regarding the hydrolysis and biodegradation of commercial fluorotelomer-based polymers (Russell et al. 2008; Koch et al. 2009; Russell et al. 2009; Washington et al. 2009a; Washington et al. 2009b) that future research will illuminate.

A number of reported observations of n:2 FTCAs and/or n:2 FTUCAs have occurred in environmental media and biota such as atmospheric particles (Stock et al. 2007), indoor dust (Barber et al. 2007), precipitation (Loewen et al. 2005; Scott et al. 2006; Taniyasu et al. 2008; Kwok et al. 2010; Scott et al. 2010), surface waters (Stock et al. 2007; Ahrens et al., 2009a; Scott et al. 2010; Zushi et al. 2011), sediments (Stock et al. 2007), WWTP effluent (Sinclair and Kannan 2006; Zushi et al. 2011), sewage sludge (Zhang et al. 2010), landfill leachate (Huset et al. 2011), animal biota (Houde et al. 2005; Taniyasu et al. 2005; Butt, Mabury, et al. 2007; Butt, Muir, et al. 2007; Furdui et al. 2007; Gebbink et al. 2009), human breast milk (So et al. 2006), and foodstuffs (Ostertag et al. 2009). The 7:3 Acid has also been detected in biota (Powley et al. 2008; Peng et al. 2010; Guruge et al. 2011). The various perfluorinated and polyfluorinated aldehydes discussed above

have apparently not yet been found in environmental samples. This is most likely due to their highly reactive nature, because only trapping experiments have qualified their presence thus far in laboratory studies.

Fluorotelomer sulfonic acids: The n:2 fluorotelomer sulfonic acids, $C_nF_{2n+1}CH_2CH_2SO_3H$ (FTSAs; Table 3) have been found in groundwater, soil, and biota, especially at military bases, firefighting training sites, and locations where major fires have been extinguished through use of AFFFs (Schultz et al. 2004; Norwegian Pollution Control Authority 2008; Oakes et al. 2010). They have also been detected in WWTP effluents (Huset et al. 2008; Ahrens et al., 2009b), landfill leachate (Eggen et al. 2010; Huset et al. 2011), precipitation and fresh surface waters (Kim and Kannan 2007; Scott et al. 2010; Nguyen et al. 2011), seawater contaminated by AFFFs (Taniyasu et al. 2005), sediments (Zushi et al. 2010), Arctic biota (Miljeteig et al. 2009), and human serum (Lee and Mabury 2011). These FTSAs arise from the degradation of more complex fluorotelomer-based substances containing the $C_nF_{2n+1}CH_2CH_2S-R$ or $C_nF_{2n+1}CH_2CH_2SO_2-R$ moiety (where R is a hydrophilic functional group that provides surfactant properties). These precursor compounds may be used as components of firefighting foams (Bertocchio and Foulletier 1970; Falk 1982; Schultz et al. 2004), e.g., the betaine $F(CF_2)_nCH_2CH_2SO_2NHCH_2CH_2N^+(CH_3)_2CH_2CH_2CO_2^-$, or in food packaging applications, e.g., the fluorotelomer mercaptoalkyl phosphate esters (Lee and Mabury 2011; Trier, Granby, et al. 2011; Trier, Nielsen, et al. 2011). FTSAs have been shown to undergo slow aerobic biotransformation to form trace levels of PFCAs (Wang et al.

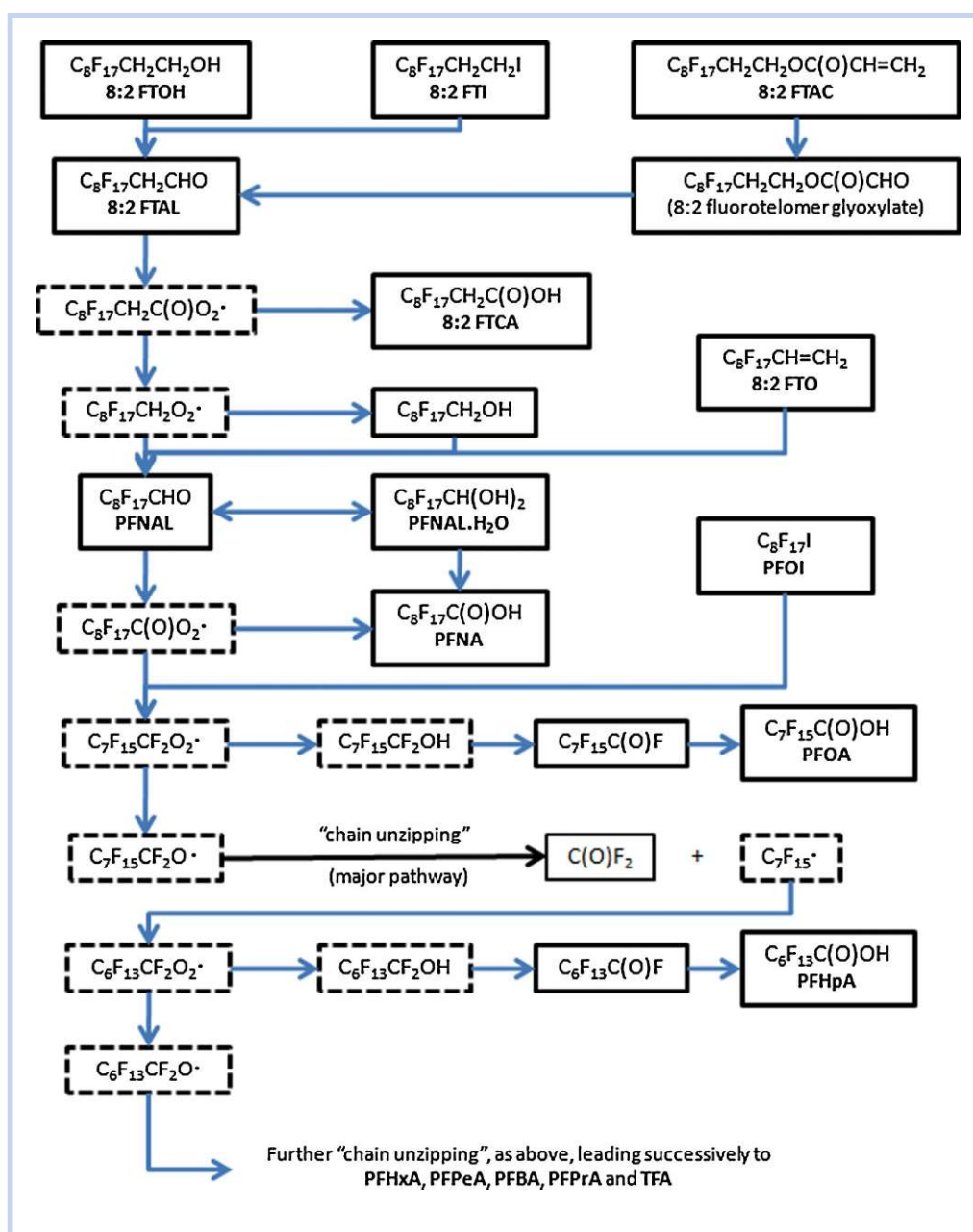


Figure 6. Simplified atmospheric degradation scheme for 8:2 fluorotelomer derivatives. Free-radical and transient molecular intermediates are shown in boxes with a dashed outline, while the starting compounds, the more stable molecular intermediates, and the final products are shown in boxes with a solid outline, their acronyms being indicated in bold type. An arrow on the chart often implies several elementary steps: i.e., certain intermediates are omitted.

2011). It should be noted that 6:2 FTSA has been referred to in some literature as “tetrahydro PFOS.” Because 6:2 FTSA is both chemically and biologically very different from PFOS (Wang et al. 2011), we strongly discourage this usage and recommend 6:2 FTSA be used in naming this substance.

Perfluoroalkane sulfonamido derivatives: Perfluoroalkane sulfonamides, sulfonamidoethanols, sulfonamidoethyl acrylates, and sulfonamidoethyl methacrylates. In the same way as the perfluoroalkyl iodides and fluorotelomer iodides are important building blocks for a broad range of fluorotelomer derivatives, the perfluoroalkane sulfonyl fluorides, $C_nF_{2n+1}SO_2F$ (PASFs; Table 2) play an analogous role as precursors in the manufacture not only of the PFSA already discussed, but also of a variety of compounds containing

the perfluoroalkane sulfonamido group, $C_nF_{2n+1}SO_2NH<$ (Tables 2 and 3). This is illustrated in Figure 7 for the synthesis of several families of perfluoroalkane sulfonamido derivatives, exemplified for a starting PASF with 8 C atoms. PFSA were directly manufactured by hydrolysis of PASFs and the various salt forms (ammonium, diethanolamine, and K and Li salts) were manufactured by neutralization of the acids. The greater part of the production of PASFs (notably POSF), however, was used to produce fluorinated surfactants and high-molecular-weight fluorinated polymeric products (3M Company 1999). The major pathway for conversion of PASFs into commercial derivatives involves reacting them in a first step with a primary amine, generally methylamine or ethylamine, to give *N*-methyl or *N*-ethyl perfluoroalkane sulfonamides, $C_nF_{2n+1}SO_2NH(C_mH_{2m+1})$, where $m = 1$ or 2